Indian Journal of Chemistry
Vol. 41B, January 2002, pp. 218-219

Note

Facile transformation of hydrazones to *N*-acylhydrazines with *m*-chloroperbenzoic acid in the solid state

K Mogilaiah*, H Ramesh Babu, R Babu Rao &
N Vasudeva Reddy

Department of Chemistry, Kakatiya University,
Warangal 506 009, India

Received 30 October 2000; accepted (revised) 6 March 2001

An efficient and simple methodology for the conversion of aryl aldehyde 3-(*p*-chlorophenyl)-1,8-naphthyridin-2-ylhydrazones **1** to *N*-aroyl-*N'*-(3-*p*-chlorophenyl-1,8-naphthyridin-2yl)hydrazines **3** using *m*-chloroperbenzoic acid (*m*-CPBA) under solid conditions is described.

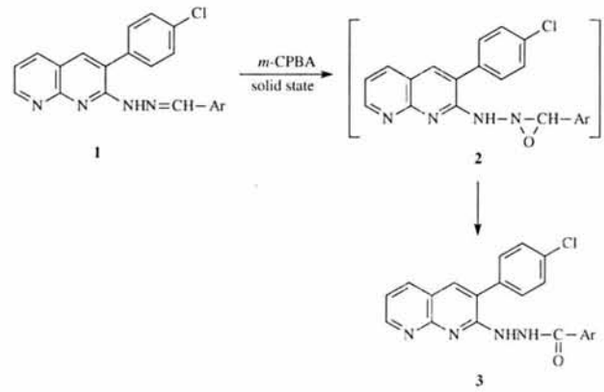
Interest in solid state organic reactions (SSOR) has increased in recent years, though reactions in solution are much more common. This is due to the fact that in many cases, ground state organic reactions occur more effectively and selectively than the solution reactions.[1-5] Developing mild and efficient methods for the oxidation of hydrazones to afford acylhydrazines continues to be a significant aspect of organic chemical transformation. In view of this and in continuation of our interest on solid state organic reactions,[6,7] herein we report a simple and efficient method for the transformation of hydrazones to *N*-acylhydrazines using *m*-chloroperbenzoic acid (*m*-CPBA) in the solid state at room temperature.

Treatment of **1**[8] with *m*-CPBA at room temperature in the solid state afforded the corresponding *N*-aroyl-*N'*-(3-*p*-chlorophenyl-1,8-naphthyridin-2-yl)hydrazines **3**. The formation of **3** can be rationalized on the basis of the initial addition of *m*-CPBA to the imine double bond followed by the cleavage of oxaziridine ring **2**. The most convincing evidence in support of the formation of **3** was provided by their IR spectra (The presence of a band around 1660 cm^{-1}, which is characteristic of the C=O stretching, proves the formation of a carbonyl group). The reaction is very facile, rapid, exothermic and efficient and is devoid of any side products. The yields are good to excellent and purity is high.

In a typical case, equimolar quantities of *m*-CPBA and hydrazone **1c** were intimately mixed together and placed at room temperature. After 3 min, a sudden exothermic reaction took place and the reaction mixture was treated with 5% $NaHCO_3$ and filtered off. After usual work-up *N*-*p*-methoxybenzoyl-*N'*-(3-*p*-chlorophenyl-1,8-naphthyridin-2-yl)hydrazine **3c** was obtained in 92% yield. Its structure was established from spectral data [IR (KBr): 3250, 3150 (NH), 1658 cm^{-1} (C=O); ^1H NMR (DMSO-d_6): δ 3.89 (s, 3H, OCH_3), 8.17 (m, 1H, C_4-H), 8.26 (m, 1H, C_5-H), 7.92 (m, 1H, C_6-H), 8.52 (m, 1H, C_7-H), 7.00-7.78 (m, 10H, NHNH and 8 Ar-H); MS: 404 (M^+, 7.2%), 389 (17.9), 386 (100), 371 (10.7), 343 (10), 255 (36.5), 254 (26.9), 240 (34.4), 239 (12.7), 228 (24.4), 205 (16.6), 164 (14.1), 150 (10.4), 149 (13.2), 135 (54.5)].

The generality of this facile transformation was established by treating other hydrazones **1** with *m*-CPBA under solid state conditions to get the corresponding *N*-aroyl- *N'*-1,8-naphthyridin-2-yl hydrazines **3** in 85-96% yields (**Scheme I, Table I**).

In conclusion, the use of *m*-CPBA permits the conversion of hydrazones into the corresponding acylhydrazines, in a new and convenient way. This method has the additional advantages of simple performance, high yields, short reaction period, easy work-up, high purity of the products and minimum environmental impact.



(Ar)				
	a,	C_6H_5	**f**,	*o*-OHC_6H_4
	b,	*p*-$CH_3C_6H_4$	**g**,	*p*-OHC_6H_4
	c,	*p*-$CH_3OC_6H_4$	**h**,	*p*-$(CH_3)_2NC_6H_4$
	d,	*p*-ClC_6H_4	**i**,	*p*-$NO_2C_6H_4$
	e,	2,4-$Cl_2C_6H_3$	**j**,	3,4-$(O\text{-}CH_2\text{-}O)C_6H_3$

Scheme I

Table I — Characterization data of compounds **3**

Compd	Reaction period (min)	m.p. °C	Yield (%)	Mol. formula	Found (%) (Calcd) C	H	N
3a	4.5	215	85	$C_{21}H_{15}N_4OCl$	67.40 (67.29	4.08 4.00	14.86 14.95)
3b	2.5	227	94	$C_{22}H_{17}N_4OCl$	67.82 (67.95	4.31 4.37	14.52 14.41)
3c	3.0	242	92	$C_{22}H_{17}N_4O_2Cl$	65.39 (65.26	4.25 4.20	13.93 13.84)
3d	2.5	216	96	$C_{21}H_{14}N_4OCl_2$	61.80 (61.61	3.49 3.42	13.78 13.69)
3e	3.0	232	88	$C_{21}H_{13}N_4OCl_3$	56.98 (56.82	2.98 2.93	12.74 12.63)
3f	3.5	205	87	$C_{21}H_{15}N_4O_2Cl$	64.68 (64.53	3.89 3.84	14.40 14.34)
3g	3.0	253	90	$C_{21}H_{15}N_4O_2Cl$	64.67 (64.53	3.88 3.84	14.42 14.34)
3h	2.0	248	89	$C_{23}H_{20}N_5OCl$	66.30 (66.11	4.86 4.79	16.88 16.77)
3i	1.5	236	86	$C_{21}H_{14}N_5O_3Cl$	60.21 (60.07	3.39 3.34	16.78 16.69)
3j	2.0	225	91	$C_{22}H_{15}N_4O_3Cl$	63.22 (63.08	3.63 3.58	13.47 13.38)

Experimental Section

Melting points are uncorrected and were taken on a Cintex melting point apparatus. IR spectra were recorded in KBr on a Perkin-Elmer spectrum BX series FT-IR spectrophotometer; ^{1}H NMR spectra on a Varian Gemini 200 MHz spectrometer using TMS as internal standard (chemical shifts in δ, ppm) and mass spectra on a Jeol JMS D-300 spectrometer operating at 70 eV. Homogeneity of the compounds was checked by TLC on silica gel plates.

General procedure for the conversion of hydrazones 2 to acylhydrazines 3. A mixture of appropriate hydrazone **1** (0.01 mole) and *m*-CPBA (0.01 mole) was kept at room temperature for the period indicated in **Table I.** After the completion of the exothermic reaction, the residue was treated with 5% $NaHCO_3$. The solid thus obtained was filtered, washed with water and recrystallized from ethanol to afford **3** (**Table I**).

Acknowledgement

The authors are thankful to the Directors, IICT, Hyderabad and CDRI, Lucknow for providing ^{1}H NMR and mass spectra, respectively.

References

1 Toda F, *Syn Lett (Account)*, **1993**, 303.
2 Toda F, *Acc Chem Res*, 28, **1995**, 480.
3 Desiraju G R & Goud B S, *Reactivity of solids: past, present and future,* edited by V V Boldyrev (Blackwell Science, London), **1994,** p. 223.
4 Toda F & Imai N, *J Chem Soc Perkin Trans 1*, **1994**, 2673.
5 Khruscheva N S, Loim N M, Sokolov V I & Makhaev V D, *J Chem Soc Perkin Trans 1*, **1997**, 2425.
6 Mogilaiah K & Rao R B, *Indian J Chem*, 38B, **1999**, 869.
7 Mogilaiah K & Rao R B, *Indian J Chem*, 39B, **2000**, 145.
8 Mogilaiah K & Chowdary D S, *Indian J Chem*, accepted for publication.